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Calix[5]arene-Based Receptor for Dumb-Bell-Shaped C_{120}

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We have developed calix[5]arene-based receptors for dumb-bell-shaped C_{120}. The receptors encapsulate C_{120} with the high binding constants in *o*-dichlorobenzene.

Fullerenes have generated a rapidly growing and active research area in the field of chemistry. Recently, the syntheses of C_{60} dimers have been intensively studied due to their unique structures.[1] The dumb-bell-shaped dimer C_{120}[2] carrying a cyclobutane ring, has been synthesized; however, poor solubility of the dimer in common organic solvents hampers studies of its chemical and physical properties. Host–guest chemistry can be helpful to overcome its low solubility. Receptors for the dimers are, however, have so far limited studies,[3] although many examples for C_{60} receptors have been reported.[4]

Over the past five years, we have developed calix[5]arene-based receptors, showing effective binding toward C_{60} and C_{70}.[5] We found that the large stabilization of the fullerene complexes is established by an accumulation of the van der Waals attraction through the effective contacts of the cavity interior to C_{60} or C_{70}. In order to produce the effective van der Waals contacts to C_{120}, a sizable cavity has to be provided. Our successful design of the receptors for C_{120} is to connect two calix[5]arenes using suitable linkers: biphenyl, *p*-diethynylphenyl, *m*-diethynylphenyl, and diacetylene groups.

The syntheses of the receptors started from calix[5]arene **5**.[5c] A palladium-mediated coupling reaction of **5** and diboronic acid **6** was proceeded in the presence of sodium carbonate in dioxane. Subsequent hydrolysis of the acetyl groups with potassium carbonate in methanol gave receptor **1** in 7% yield. Sonogashira's coupling reaction of **5** and *p*-diethynylbenzene **7**[6] with diisopropylamine in THF and subsequent deprotection of the acetyl groups afforded receptor **2** in 44% yield.

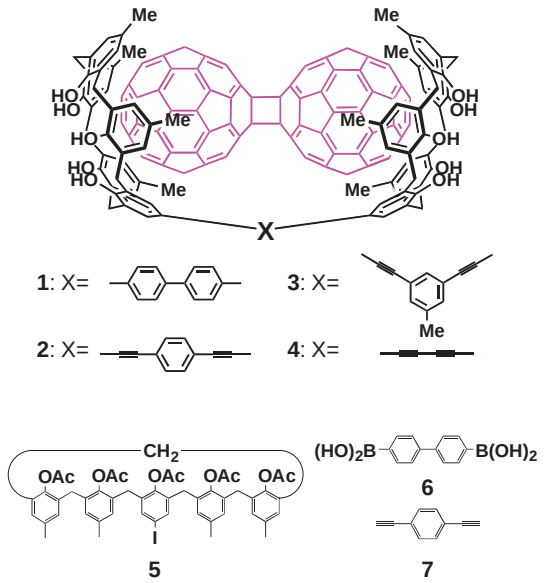

Chart 1.

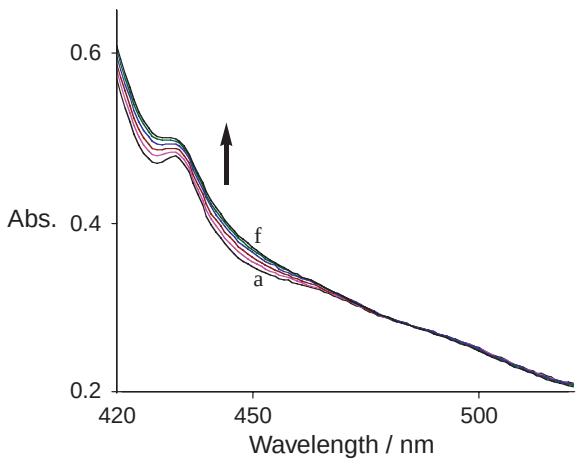

Fig. 1. Absorption spectra of C_{120} (6.90×10^{-5} mol L^{-1}) in the presence of **1** in ODCB. The concentrations of **1** are from the bottom (curves (a)–(f)), 0.0, 0.72, 1.44, 2.16, 2.88, and 3.60 ($\times 10^{-4}$ mol L^{-1}).

The binding of C_{120} to the receptors was studied in *o*-dichlorobenzene (ODCB) by the standard titration technique using UV–vis spectroscopy. Upon the addition of a stock solution of **1** to a C_{120} solution, the intensity of the shoulder around the 430 nm region increased (Fig. 1). This indicates host–guest complex formation between **1** and C_{120}. The isosbestic point at 483 nm as well as Job's plot provided evidence of a 1:1 complex in solution (Figs. 1 and 2).[7a] Plotting of the spectral changes vs the receptor concentrations afforded a hyperbolic curve. A non-linear least-squares regression analysis[7b] gave the binding constant (Ka: 2700 ± 300 dm^3 mol^{-1}). The bind-

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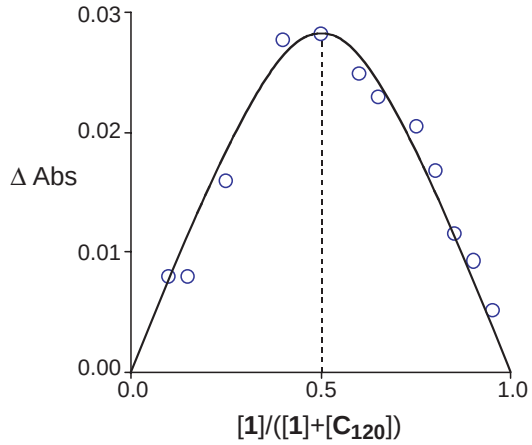

Fig. 2. Job's plot of **1** for C_{120} in ODCB.

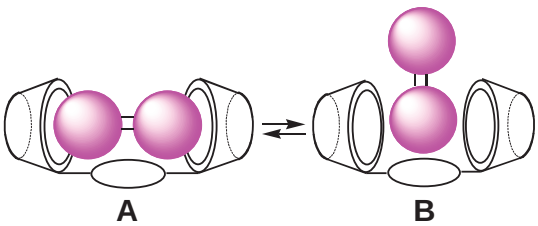

Fig. 3. The possible binding modes of C_{120} for the receptors.

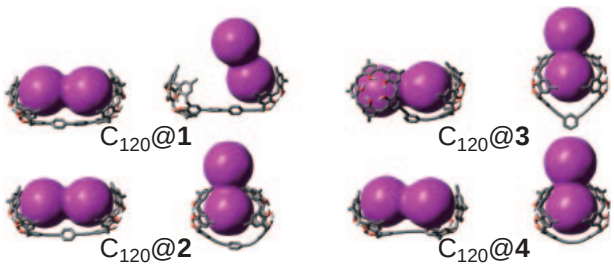

Fig. 4. The calculated structures of the conformers A and B.

ing constants for the other hosts were determined in a similar manner (*K*a: 10700 ± 700, 3900 ± 600, and 12300 ± 600 $dm^3\,mol^{-1}$ for **2**, **3**, and **4**).

The extended cavities of the receptors effectively encapsulate a C_{120} molecule with high binding constants in ODCB. Strong complexations were attained by **2** and **4**. Their binding abilities were ca. 3–5-fold higher than those found in **1** and **3**.

There are the two possible binding modes in the host–guest complexes: one is conformation A, in which both C_{60} moieties situate within the calix[5]arenes; in the other, conformation B, only one of the C_{60} moieties is wrapped up by the two calix[5]-arenes (Fig. 3). While precise solution structures remain to be determined, molecular mechanics calculations of the complexes are informative. The molecular mechanics calculations were carried out using the AMBER* force field, as implemented in MacroModel[8] V.6.5, together with the GB/SA solvation model of chloroform.

Judging from the calculation (Fig. 4), the accommodation of the guest in conformation B should pay considerable energetic costs for **1**[9] and **2**, leading to significant energy differences between conformers A and B (ΔSE_{A-B}: -123 and -100 $kJ\,mol^{-1}$ for **1** and **2**, respectively). This result suggests that complexes of **1** and **2** dominantly adopt conformation A. In contrast, both conformations A and B can be present in complexes of **3** and **4** based on the smaller energy differences (ΔSE_{A-B}: -47 and 0 $kJ\,mol^{-1}$ for **3** and **4**, respectively). This might be supported by the fact that **3** and **4** are good hosts for C_{60}.[5d]

In conclusion, we developed a new class of the receptors for dumb-bell-shaped C_{120}. The receptors should be helpful for overcoming the poor solubility of C_{120}.

Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury-300, JEOL Lambda-500, and ECA-600 spectrometers. The chemical shifts are reported in parts per million (δ, ppm) relative to the solvent residual. FAB mass spectra were measured on a JEOL Type SX-102.

Double Calix[5]arene 1. To a mixture of **5** (400 mg, 0.43 mmol), **6** (50 mg, 0.21 mmol) in dioxane (8 mL) and ethanol (3 mL) were added [$Pd(PPh_3)_4$] (74 mg, 0.06 mmol) and 2 M Na_2CO_3 (0.3 mL). After refluxing the mixture for 7 h, the solution was filtered. After concentration in vacuo, the residue was dissolved in methanol (20 mL) and THF (5 mL), and then potassium carbonate (500 mg, 3.62 mmol) was added to the solution. After being stirred for 2 h at room temperature, the mixture was poured into 1 M HCl, extracted with chloroform, and dried over Na_2SO_4. The organic layer was concentrated and the residue was purified by column chromatography on silica gel to give desired compound **1** (19 mg, 7%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.82 (brs, 10H), 7.69 (ABq, 4H, $J = 7.8$ Hz), 7.62 (ABq, 4H, $J = 7.8$ Hz), 7.45 (s, 4H), 7.04 (s, 4H), 7.01 (s, 4H), 6.99 (s, 8H), 3.76 (m, 20H), 2.24 (s, 24H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 150.1, 147.9, 147.9, 139.9, 139.3, 134.2, 130.8, 130.7, 129.9, 129.7, 129.1, 128.3, 127.9, 127.4, 127.4, 126.7, 126.6, 126.5, 126.3, 31.7, 31.5, 20.5, 20.5. FAB MS (NBA) m/z 1323 ($[M + H]^+$). HR MS m/z 1323.5964 ($[M + H]^+$, $C_{90}H_{83}O_{10}$, calcd 1323.5986).

Double Calix[5]arene 2. To a mixture of **5** (1.5 g, 1.6 mmol), CuI (60 mg, 0.32 mmol) in THF (15 mL) were added diisopropylamine (11 mL, 78 mmol), [$Pd(PPh_3)_4$] (370 mg, 0.32 mmol) and *p*-diethynylbenzene (100 mg, 0.79 mmol). After being stirred for 1 h, the reaction mixture was poured into 1 M HCl, extracted with chloroform, and dried over Na_2SO_4. The residue was dissolved in methanol (20 mL) and THF (5 mL), and then potassium carbonated (1.0 g, 7.3 mmol) was added. After being stirred for 1 h, the mixture was poured into 1 M HCl, extracted with chloroform and dried over Na_2SO_4. The residue was purified by column chromatography on silica gel to give the desired compound **2** (450 mg, 44%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.30 (s, 2H), 8.78 (s, 4H), 8.71 (s, 4H), 7.49 (s, 4H), 7.40 (s, 4H), 7.00–6.99 (m, 16H), 3.78 (m, 20H), 2.24 (s, 24H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 151.1, 147.9, 147.8, 132.7, 132.5, 131.5, 131.0, 130.8, 129.9, 129.8, 127.3, 126.7, 126.6, 126.5, 125.8, 123.1, 115.8, 91.3, 88.0, 31.4, 31.4, 31.3, 20.5. FAB MS (NBA) m/z 1295 ($[M + H]^+$). HR MS m/z 1295.5664 ($[M + H]^+$, $C_{88}H_{79}O_{10}$, calcd 1295.5673).

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9 The 1:2 complex formation of receptor **1** with two C_{60} molecules was confirmed by Job's plot.